Chemistry 2740 Spring 2008 Test 3

Time: 50 min	**Questions:** 4	**Marks:** 40
Aids permitted: calculator, one 8.5×11-inch formula sheet		

1. Briefly explain the relationship between the law of microscopic reversibility and the concept of dynamic equilibrium. [5 marks]

2. Describe two different methods for obtaining a pressure jump and discuss briefly their relative advantages and disadvantages. [10 marks]

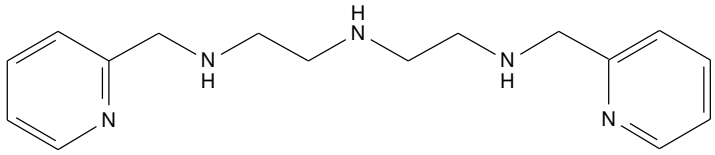
   Note: Diagrams are often helpful in questions like these.

3. The reactions of chelated nickel(II) ion complexes with acetonitrile have been studied in the gas phase.[1] In the following reaction, L represents a ligand. The acetonitrile (CH_3CN) is a Lewis base which forms a coordinate bond directly to the nickel(II) ion.

$$NiL^{2+} + CH_3CN \underset{k_d}{\overset{k_a}{\rightleftharpoons}} [NiL^{2+} \cdot CH_3CN]$$

   (a) At 300 K with the ligand illustrated below, the following data were obtained:

$$\begin{aligned} k_a &= 2.4 \times 10^{11}\,\mathrm{L\,mol^{-1}s^{-1}} \\ K &= 8.1 \times 10^{12}\,\mathrm{L/mol} \end{aligned}$$



   (K is the empirical equilibrium constant for the reaction.) Calculate k_d. [2 marks]

   (b) Suppose that we start off with 1.7×10^{-11} mol/L of acetonitrile and 1.0×10^{-11} mol/L of NiL^{2+}. What is the initial rate of reaction? [2 marks]

   (c) Approximately how long would it take to accumulate 1×10^{-14} mol/L of product under the conditions described above? [2 marks]

[1] M. Y. Combariza and R. W. Vachet, *J. Am. Soc. Mass Spectrom.* **15**, 1128 (2004).

4. There is a great deal of interest in oxidative damage to polymers. This has led to a series of studies on the reactions of polymers with radicals. One such study examined the kinetics of the radical 1,1-diphenyl-2-picrylhydrazyl (DPPH) with polyphenylene (PP).[2]

   (a) Typically, polymers react with two equivalents of a radical to yield products without unpaired electrons. The authors of this study proposed the following mechanism:

$$\mathrm{PP} + \mathrm{DPPH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{\mathrm{PP} \cdot \mathrm{DPPH}\}$$
$$\{\mathrm{PP} \cdot \mathrm{DPPH}\} + \mathrm{DPPH} \xrightarrow{k_2} \text{products}$$

   Develop a rate law for the reaction based on this mechanism. Under what conditions would a simple second-order dependence on the DPPH concentration be observed? [10 marks]

   (b) In the presence of an excess of polyphenylene at 65°C, the following data were obtained:

t/min	2.7	14.6	26.5	38.2
$[\mathrm{DPPH}]/10^{-5}\,\mathrm{mol\,L^{-1}}$	8.50	5.58	4.40	3.59

   Are these data consistent with a second-order reaction? If so, what is the rate constant? [9 marks]

[2] V. A. Vonsyatskii, G. I. Kalyaev and A. A. Berlin, *React. Kinet. Catal. Lett.* **61**, 280 (1997).